

(12) **UK Patent Application** (19) **GB** (11) **2 269 004** (13) **A**

(43) Date of A Publication 26.01.1994

(21) Application No 9314740.3

(22) Date of Filing 16.07.1993

(30) Priority Data

(31) 9215684

(32) 23.07.1992

(33) GB

(51) INT CL⁵

F25B 45/00, C09K 5/04

(52) UK CL (Edition M)

F4H HGXJ

C4X X2A

(71) Applicant(s)

Imperial Chemical Industries PLC

(Incorporated in the United Kingdom)

Imperial Chemical House, Millbank, LONDON,
SW1P 3JF, United Kingdom

(56) Documents Cited

None

(58) Field of Search

UK CL (Edition L) F4H HGXJ

INT CL⁵ F25B

ONLINE DATABASE:WPI

(72) Inventor(s)

Stuart Corr

(74) Agent and/or Address for Service

Anthony Robert Collingwood

Imperial Chemical Industries PLC, ICI Group Patents,

Group Patents Services Dept. PO Box 6, Shire P Park,

Bessemer Road, WELWYN GARDEN CITY,

Hertfordshire, AL7 1HD, United Kingdom

(54) A method of replacing the working fluid in a heat transfer device.

(57) A method for replacing a first working fluid composition held within a heat transfer device by a second working fluid composition, wherein the first working fluid composition comprises a first heat transfer fluid and a first lubricant and the second working fluid composition comprises a second heat transfer fluid comprising at least one fluoroalkane and a second lubricant. The first lubricant may be a mineral oil, and the second lubricant may be polyoxyalkylene glycol. The first heat transfer fluid may comprise chlorodifluoromethane. The second heat transfer fluid may comprise at least one of difluoromethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, 1,1-difluoroethane, 1,1,1-trifluoroethane and 1,1,2-trifluoroethane.

BEST AVAILABLE COPY

GB 2 269 004 A

WORKING FLUID REPLACEMENT METHOD.

This invention relates to a method of replacing a working fluid composition within a heat transfer device.

Heat transfer devices of the mechanical vapour recompression type, including refrigerative, heat pump and air conditioning systems, are well known. The chlorofluorocarbon and hydrochlorofluorocarbon heat transfer fluids which are presently used in these devices such as dichlorodifluoromethane (R-12) and chlorodifluoromethane (R-22) have been implicated in the destruction of the stratospheric ozone layer. As a result, the production and use of these compounds is to be severely restricted by international agreement.

Newly manufactured heat transfer devices will thus utilise so-called "ozone friendly" heat transfer fluids, for example heat transfer fluids comprising one or more fluoroalkanes such as 1,1,1,2-tetrafluoroethane (R-134a), 1,1,2,2-tetrafluoroethane (R-134), difluoromethane (R-32), pentafluoroethane (R-125), 1,1-difluoroethane (R-152a), 1,1,1-trifluoroethane (R-143a) and 1,1,2-trifluoroethane (R-143).

The replacement of a non-ozone friendly heat transfer fluid contained within an existing device is also thought to be desirable in order to avoid leaks of such a fluid into the atmosphere and to allow for the controlled disposal thereof. Unfortunately, simple replacement of a non-ozone friendly heat transfer fluid with an ozone friendly heat transfer fluid is not practicable, since the lubricant which is generally used in association with such a non-ozone friendly heat transfer fluid, e.g. a mineral oil, is not usually

compatible with the replacement ozone friendly heat transfer fluid.

5 A method of replacing a non-ozone friendly heat transfer fluid and the lubricant associated therewith with an ozone friendly heat transfer fluid and a new lubricant has now been devised. The method allows for the removal of substantially all of the original lubricant and its replacement with a new lubricant which is compatible with the replacement ozone friendly heat transfer fluid.

10 Accordingly, there is provided a method for replacing a first working fluid composition held within a heat transfer device by a second working fluid composition, wherein the first working fluid composition comprises a first heat transfer fluid and sufficient to provide lubrication of a first lubricant and the second working fluid composition comprises a second heat transfer fluid comprising at least one fluoroalkane and sufficient to provide lubrication of a second lubricant which is compatible with both the first and second heat transfer fluids, which method comprises sequentially performing the steps

- (a) discharging from the device a volume of a lubricant;
- 25 (b) charging to the device sufficient of the second lubricant to maintain lubrication;
- (c) circulating the second lubricant within the device;
- (d) optionally assaying the residue of the first lubricant within the device;
- 30 (e) repeating steps (a) to (d) as necessary until an acceptably low concentration of the first lubricant remains in the device; thereafter

(f) discharging from the device the first heat transfer fluid and charging to the device sufficient of the second heat transfer fluid to provide an adequate heat transfer effect.

5 The first heat transfer fluid may be any of the chlorofluorocarbon and/or hydrochlorofluorocarbon containing heat transfer fluids which are presently in use in commercial refrigeration systems and related heat transfer devices. Specific mention may be made of
10 dichlorodifluoromethane (R-12), chlorodifluoromethane (R-22), 1-chloro-1,2,2,2-tetrafluoroethane (R-124), 1-chloro-1,1,2,2-tetrafluoroethane (R-124a), 1-chloro-1,1-difluoroethane (R-142b), 1-chloro-1,2,2-trifluoroethane (R-133),
15 1,1-dichloro-2,2,2-trifluoroethane (R-123), 1,2-dichloro-1,1,2-trifluoroethane (R-123a) and the azeotrope of R-22 and chloropentafluoroethane (R-115), the azeotrope being refrigerant R-502. In a preferred embodiment, the method of the present invention is
20 concerned with the replacement of a working fluid composition comprising R-22 or R-502 as the refrigerant.

 The second heat transfer fluid comprises at least one fluoroalkane. Suitable fluoroalkanes may be
25 selected from the fluoroalkanes which have been suggested as replacements for the chlorofluorocarbon and hydrochlorofluorocarbon refrigerants presently in use such as R-12, R-22 and R-502. Preferred fluoroalkanes are selected from the group consisting of
30 difluoromethane (R-32), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), 1,1-difluoroethane (R-152a), 1,1,1-trifluoroethane (R-143a) and 1,1,2-trifluoroethane (R-143).

The second heat transfer fluid may comprise one, two, three or more fluoroalkanes. Where the second heat transfer fluid comprises a single fluoroalkane, it is preferably R-134a.

5 As stated above, the method of the present invention is particularly concerned with the replacement of a working fluid composition comprising R-22 or R-502 as the refrigerant. A particularly desirable second heat transfer fluid for replacing R-22
10 or R-502 is one which comprises a mixture of:

- (1) tetrafluoroethane;
- (2) at least one fluoroalkane selected from the group consisting of difluoromethane (R-32) and 1,1,1-trifluoroethane (R-143a); and optionally
15 (3) pentafluoroethane (R-125).

The tetrafluoroethane may be 1,1,1,2-tetrafluoroethane (R-134a) or 1,1,2,2-tetrafluoroethane (R-134) or a mixture of these two isomers. Preferably, however, the tetrafluoroethane is a single isomer, and more
20 preferably is R-134a.

Although such a second heat transfer fluid may comprise more than three components, it is preferably a binary or ternary mixture. The mixture may be an azeotrope or near-azeotrope, but will normally be
25 zeotropic.

In one particularly preferred embodiment of the present invention in which the working fluid composition to be replaced comprises R-22 as the refrigerant, the second heat transfer fluid is a binary
30 mixture of R-134a and R-32. Preferably, such a mixture comprises from 45 to 75 % by weight, more preferably from 65 to 75 % by weight of R-134a and the complementary percentage by weight of R-32. A particularly preferred binary mixture comprises about
35

70 % by weight of R-134a and about 30 % by weight of R-32.

5 In a further preferred embodiment of the present invention in which the working fluid composition to be replaced comprises R-22 or R-502 as the refrigerant, the second heat transfer fluid comprises a ternary or higher mixture of:

- (1) R-134a or R-134;
- 10 (2) at least one fluoroalkane selected from the group consisting of R-32 and R-143a; and optionally
- (3) R-125.

Particularly suitable ternary heat transfer fluids for replacing refrigerants R-22 and R-502 may be
15 selected from:

- (a) R-134a + R-32 + R-143a;
- (b) R-134 + R-32 + R-143a;
- (c) R-134a + R-32 + R-125;
- (d) R-134 + R-32 + R-125;
- 20 (e) R-134a + R-143a + R-125; and
- (f) R-134 + R-143a + R-125.

A particularly preferred second heat transfer fluid for replacing refrigerants R-22 and R-502 comprises a mixture of:

- 25 (1) R-134a or R-134, especially R-134a;
- (2) R-32 or R-143a, especially R-32; and
- (3) R-125.

One particularly preferred second heat transfer fluid for replacing R-22 is a ternary mixture
30 consisting of:

- (1) 55 to 65 % by weight, particularly about 60 % by weight of R-134a;
- (2) 25 to 35 % by weight, particularly about 30 % by weight of R-32; and

(3) 5 to 15 Z by weight, particularly about 10 Z by weight of R-125.

Another particularly preferred second heat transfer fluid for replacing R-22 is a ternary mixture consisting of:

(1) 25 to 35 Z by weight, particularly about 30 Z by weight of R-134a;

(2) 45 to 55 Z by weight, particularly about 50 Z by weight of R-32; and

(3) 15 to 25 Z by weight, particularly about 20 Z by weight of R-125.

One particularly preferred second heat transfer fluid for replacing R-502 is a ternary mixture consisting of:

(1) 45 to 55 Z by weight, particularly about 50 Z by weight of R-134a;

(2) 25 to 35 Z by weight, particularly about 30 Z by weight of R-32; and

(3) 15 to 25 Z by weight, particularly about 20 Z by weight of R-125.

Another particularly preferred second heat transfer fluid for replacing R-502 is a ternary mixture consisting of:

(1) 45 to 55 Z by weight, particularly about 50 Z by weight of R-134a;

(2) 35 to 45 Z by weight, particularly about 40 Z by weight of R-32; and

(3) 5 to 15 Z by weight, particularly about 10 Z by weight of R-125.

All the percentages by weight quoted above are based on the total weight of the second heat transfer fluid.

The first lubricant may be any of the lubricants which are presently employed in commercial heat

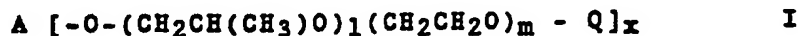
transfer devices. Typically, the first lubricant is a mineral oil, a synthetic hydrocarbon, e.g. an alkyl benzene, or a blend of these materials. More typically, the first lubricant is a mineral oil.

5 The second lubricant may be any which is compatible with the first and second heat transfer fluids. Preferably, the second lubricant is also miscible with the first lubricant.

10 The second lubricant may, for example, be selected from the synthetic lubricants which have been developed for use with the replacement ozone friendly heat transfer fluids such as R-134a.

15 Suitable second lubricants may be selected from the polyoxyalkylene glycols. Suitable polyoxyalkylene glycol lubricants include hydroxyl group initiated polyoxyalkylene glycols, e.g. ethylene and/or propylene oxide oligomers/polymers initiated on mono- or polyhydric alcohols such as methanol, butanol, pentaerythritol and glycerol. Such polyoxyalkylene
20 glycols may also be end-capped with suitable terminal groups such as alkyl, e.g. methyl groups.

25 A particular polyoxyalkylene glycol lubricant is one having an average molecular weight in the range of from about 150 to about 3000 and comprising one or more compounds of general formula:



30 wherein

A is the residue remaining after removing the hydroxyl groups from a hydroxyl containing organic compound;

Q represents an optionally substituted alkyl, aralkyl or aryl group;

l and m are independently 0 or an integer provided that at least one of l or m is an integer; and

5 x is an integer.

The polyoxyalkylene glycol lubricant may be prepared using conventional techniques. Such techniques are well known to those skilled in the art. Thus, in one method a hydroxyl containing organic compound such as an alcohol is reacted with ethylene oxide and/or propylene oxide to form an ethylene oxide and/or propylene oxide oligomer/polymer containing terminal hydroxyl groups which is subsequently etherified to give a polyoxyalkylene glycol of Formula I. The polyoxyalkylene glycol lubricant which is finally formed will not usually consist of a single compound of Formula I, but will usually comprise a mixture of such compounds which vary from one another in respect of the degree of polymerisation, i.e. the number of ethylene and/or propylene oxide residues. Moreover, a mixture of alcohols and/or phenols may be used as initiators in the formation of the polyoxyalkylene glycol lubricant, and a mixture of etherifying agents which provide different Q groups may also be used. The molecular weight of a polyoxyalkylene glycol lubricant comprising a mixture of compounds of Formula I will represent the average molecular weight of all the compounds present, so that a given lubricant may contain specific polyoxyalkylene glycols which have a molecular weight outside the range quoted above, providing that the average molecular weight of all the compounds is within that range.

The moiety A in the polyoxyalkylene glycol of Formula I is the residue remaining after removing the

hydroxyl groups from a hydroxyl containing organic compound. Such compounds include the mono- and polyhydric alcohols and phenols. Where the hydroxyl containing organic compound which is used as an initiator in the formation of the polyoxyalkylene glycol is a monohydric alcohol or phenol, A is preferably a hydrocarbyl group and more preferably is an alkyl, aryl, alkaryl or aralkyl group, especially alkyl. Suitable alkyl groups for A may be selected from the straight chain (linear), branched or cyclic alkyl groups. Preferably, A is a C₁₋₁₂, particularly a C₁₋₁₀ and especially a C₁₋₆ alkyl group. Specific examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, the various pentyl groups, the various hexyl groups, cyclopentyl, cyclohexyl and the like. Particularly preferred alkyl groups for A are the C₁₋₁₂, particularly the C₁₋₁₀ and especially the C₁₋₆ straight chain alkyl groups, examples of which have been listed above. An especially preferred alkyl group for A is methyl or n-butyl.

Other suitable hydrocarbyl groups for A are those which remain after removing a hydroxyl group(s) from benzyl alcohol and phenols such as phenol, cresol, nonylphenol, resorcinol and bisphenol A.

Where a polyhydric alcohol is used in the formation of the polyoxyalkylene glycol, A is preferably a hydrocarbon radical. Suitable hydrocarbon radicals for A are those which remain after removing the hydroxyl groups from polyhydric alcohols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, cyclohexane dimethanol, glycerol, 1,2,6-hexane triol, trimethylolpropane, pentaerythritol, dipentaerythritol

and sorbitol. A particularly preferred hydrocarbon radical for A is that remaining after removing the hydroxyl groups from glycerol.

5 The moiety Q in the polyoxyalkylene glycol of Formula I is an optionally substituted alkyl, aralkyl or aryl group. A preferred optionally substituted aralkyl group for Q is an optionally substituted benzyl group. Preferred optionally substituted aryl groups for Q include phenyl and alkyl substituted phenyl groups.
10 Preferably, Q is an optionally substituted, for example halogen substituted, alkyl group, particularly an optionally substituted C₁₋₁₂ alkyl group and more particularly an optionally substituted C₁₋₄ alkyl group. Suitable alkyl groups for Q may be selected from
15 the straight chain (linear), branched or cyclic alkyl groups, especially the linear alkyl groups. Although the alkyl groups for Q are described as being optionally substituted, they are preferably unsubstituted. Accordingly, particularly preferred
20 alkyl groups for Q are selected from methyl, ethyl, propyl, isopropyl and the various butyl groups. An especially preferred alkyl group for Q is methyl.

 The polyoxyalkylene glycol of Formula I may be a polyoxyethylene glycol, a polyoxypropylene glycol or a
25 poly(oxyethylene/oxypropylene) glycol. In the latter case, the ethylene and propylene oxide residues may be arranged randomly or in blocks along the polymer chain. Preferred polyoxyalkylene glycols are the polyoxypropylene glycols and the
30 poly(oxyethylene/oxypropylene) glycols.

 Preferred second lubricants are those selected from the class known as neopentyl polyol esters. Suitable neopentyl polyol esters include the esters of pentaerythritol, polypentaerythritols such as di- and

tripentaerythritol, trimethylol alkanes such as trimethylol ethane and trimethylol propane, and neopentyl glycol. Such esters may be formed with linear and/or branched aliphatic carboxylic acids, such as
5 linear and/or branched alkanolic acids, or esterifiable derivatives thereof. A minor proportion of an aliphatic polycarboxylic acid, e.g. an aliphatic dicarboxylic acid, or an esterifiable derivative thereof may also be used in the synthesis of the ester lubricant in order
10 to increase the viscosity thereof. However, where such an aliphatic polycarboxylic acid (or esterifiable derivative thereof) is employed in the synthesis, it will preferably constitute no more than 30 mole %, more preferably no more than 10 mole % of the total amount
15 of carboxylic acids (or esterifiable derivatives thereof) used in the synthesis. Usually, the amount of the carboxylic acid(s) (or esterifiable derivative thereof) which is used in the synthesis will be sufficient to esterify all, or substantially all, of
20 the hydroxyl groups contained in the polyol, but in certain circumstances residual hydroxyl functionality may be acceptable.

A preferred neopentyl polyol ester lubricant is one comprising one or more compounds of general
25 formula:



30 wherein

R is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol, or the

35

hydroxyl containing hydrocarbon radical remaining after removing a proportion of the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol;

each R^1 is independently H, a straight chain (linear) aliphatic hydrocarbyl group, a branched aliphatic hydrocarbyl group, or an aliphatic hydrocarbyl group (linear or branched) containing a carboxylic acid or carboxylic acid ester substituent, provided that at least one R^1 group is a linear aliphatic hydrocarbyl group or a branched aliphatic hydrocarbyl group; and

n is an integer of at least 1.

The aliphatic hydrocarbyl groups specified for R^1 above may be substituted, e.g. by pendant atoms or groups such as chloro, fluoro and bromo, and/or by in chain hetero atoms such as oxygen and nitrogen. Preferably, however, such hydrocarbyl groups are unsubstituted and, except in the case where R^1 is an aliphatic hydrocarbyl group containing a carboxylic acid or carboxylic acid ester substituent, contain only carbon and hydrogen atoms.

The ester lubricants of Formula II may be prepared by reacting the appropriate polyol or mixture of polyols with the appropriate carboxylic acid or mixture of acids. Esterifiable derivatives of the carboxylic acids may also be used in the synthesis, such as the acyl halides, anhydrides and lower alkyl esters thereof. Suitable acyl halides are the acyl chlorides and suitable lower alkyl esters are the methyl esters. Aliphatic polycarboxylic acids, or esterifiable derivatives thereof, may also be used in the synthesis of the ester lubricant. Where an aliphatic

polycarboxylic acid is used in the synthesis of the ester lubricant, the resulting lubricant will comprise one or more compounds of Formula II in which at least one of the R^1 groups is an aliphatic hydrocarbyl group (linear or branched) containing a carboxylic acid or carboxylic acid ester substituent. The ability of polycarboxylic acids to react with two or more alcohol molecules provides a means of increasing the molecular weight of the ester formed and so a means of increasing the viscosity of the lubricant. Examples of such polycarboxylic acids include maleic acid, adipic acid and succinic acid, especially adipic acid. Generally, however, only monocarboxylic acids (or esterifiable derivatives thereof) will be used in the synthesis of the ester lubricant, and where polycarboxylic acids are used they will be used together with one or more monocarboxylic acids (or esterifiable derivatives thereof) and will constitute only a minor proportion of the total amount of carboxylic acids used in the synthesis. Where an aliphatic polycarboxylic acid (or an esterifiable derivative thereof) is employed in the synthesis, it will preferably constitute no more than 30 mole %, more preferably no more than 10 mole % of the total amount of carboxylic acids used in the synthesis, with one or more monocarboxylic acids (or esterifiable derivatives thereof) constituting the remainder.

Usually, the amount of the carboxylic acid(s) (or esterifiable derivative thereof) which is used in the synthesis will be sufficient to esterify all, or substantially all, of the hydroxyl groups contained in the polyol(s), in which case the lubricant will comprise one or more ester compounds of Formula II in which R is the hydrocarbon radical remaining after

removing the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol.

However, in certain circumstances ester lubricants which comprise residual hydroxyl functionality may be acceptable. Such lubricants comprise one or more ester compounds of Formula II in which R is the hydroxyl containing hydrocarbon radical remaining after removing a proportion of the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol. Esters containing residual (unreacted) hydroxyl functionality are often termed partial esters, and lubricants containing them may be prepared by utilising an amount of the carboxylic acid or acids which is insufficient to esterify all of the hydroxyl groups contained in the polyol or polyols.

It will be appreciated that the preferred neopentyl polyol ester lubricants may comprise a single compound of Formula II, i.e. the reaction product which is formed between a single polyol and a single monocarboxylic acid. However, such ester lubricants may also comprise a mixed ester composition comprising two or more compounds of Formula II. Such mixed ester compositions may be prepared by utilising two or more polyols and/or two or more carboxylic acids (or esterifiable derivatives thereof) in the synthesis of the ester, or by combining a mixture of different esters each of which is the reaction product of a particular polyol and a particular carboxylic acid. Furthermore, different mixed ester compositions, each of which has been prepared by utilising two or more polyols and/or two or more carboxylic acids (or

esterifiable derivatives thereof) in their synthesis, may also be blended together.

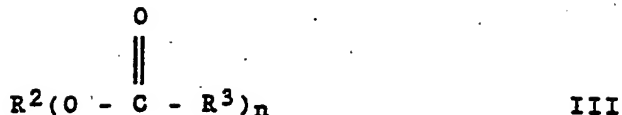
5 The preferred neopentyl polyol ester lubricants comprise one or more compounds of Formula II in which R is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol, dipentaerythritol, trimethylol propane or neopentyl glycol. Particularly preferred alcohols for the synthesis of the ester are pentaerythritol, 10 dipentaerythritol and trimethylol propane.

Preferably, each R^1 in Formula II is, independently, a linear aliphatic hydrocarbyl group or a branched aliphatic hydrocarbyl group.

15 Preferred linear aliphatic hydrocarbyl groups for R^1 are the linear alkyl groups, particularly the C_{3-10} linear alkyl groups, more particularly the C_{4-10} linear alkyl groups and especially the C_{4-7} linear alkyl groups. Examples of suitable linear alkyl groups include n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 20 n-nonyl and n-decyl.

Preferred branched aliphatic hydrocarbyl groups for R^1 are the branched alkyl groups, particularly the C_{4-14} branched alkyl groups, more particularly the C_{6-12} branched alkyl groups and especially the C_{7-9} 25 branched alkyl groups. Examples of suitable branched alkyl groups include isobutyl, isopentyl, isohexyl, isoheptyl, isooctyl, isononyl, neopentyl, neoheptyl and the branched alkyl groups contained in 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid and commercially 30 available branched C_{8-10} carboxylic acid mixtures.

Particularly preferred second lubricants are neopentyl polyol esters comprising one or more compounds of general formula:



5 wherein

R² is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol, dipentaerythritol or trimethylol propane;

10 each R³ is independently a linear alkyl group or a branched alkyl group; and

n is an integer of 3, 4 or 6,

wherein one or more of the named polyols, one or more linear alkanolic acids, or esterifiable derivatives thereof, and optionally one or more branched alkanolic acids, or esterifiable derivatives thereof, are
15 utilised in the synthesis of the ester lubricant.

Preferably, a mixture of two or more linear alkanolic acids, in particular two, or esterifiable derivatives thereof, are utilised in the synthesis of
20 the ester lubricant of Formula III. More preferably, a mixture of one or more linear alkanolic acids, or esterifiable derivatives thereof, and one or more branched alkanolic acids, or esterifiable derivatives thereof, are utilised in the synthesis. Thus,
25 particularly preferred ester lubricants are mixed ester compositions which comprise a plurality of compounds of Formula III.

Where a mixture of linear and branched alkanolic acids (or esterifiable derivatives thereof) are
30 utilised in the synthesis of the ester lubricant, as is preferred, the linear alkanolic acid(s) preferably constitutes at least 25 mole %, e.g. from 25 to 75 mole %, of the total amount of carboxylic acids used. In this way, at least 25 mole %, e.g. from 25 to 75

35

mole Z, of the hydroxyl groups contained in the polyol or mixture of polyols may be reacted with the said linear alkanolic acid(s).

5 Ester lubricants comprising one or more compounds of Formula III provide a particularly good balance between the properties desired of a lubricant and, in particular, exhibit good thermal stability, good hydrolytic stability and acceptable solubility and miscibility with the second heat transfer fluid. As
10 stated previously, the present invention is particularly concerned with a method for replacing an existing working fluid composition comprising R-22 or R-502 as the refrigerant. Refrigeration systems which contain replacements for R-22 and R-502 typically
15 operate at temperatures above those using R-134a as the sole replacement refrigerant. Thus, it is particularly desirable that the lubricant which is used in a working fluid composition designed to replace the existing compositions based on R-22 and R-502 exhibits good
20 thermal stability.

Preferably, R^2 is the hydrocarbon radical remaining after removing the hydroxyl groups from pentaerythritol or dipentaerythritol.

25 Preferred linear and branched alkyl groups for R^3 are those described above in connection with R^1 and are derived by utilising the corresponding alkanolic acids or esterifiable derivatives thereof. The preferred acids for the synthesis of the ester are selected from the group consisting of pentanoic acid, heptanoic acid
30 and branched C_8-10 alkanolic acids. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

An especially preferred ester lubricant is a mixed ester composition which comprises a plurality of

compounds of Formula III and which is the reaction product of pentaerythritol, heptanoic acid and a mixture of branched C₈₋₁₀ alkanolic acids. Preferably, the heptanoic acid will constitute from 25 to 75 mole % of the total amount of acids utilised in the synthesis, with the branched C₈₋₁₀ acids constituting the remainder. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

Another especially preferred ester lubricant is a mixed ester composition which comprises a plurality of compounds of Formula III and which is the reaction product of pentaerythritol, dipentaerythritol, heptanoic acid and a branched C₉ alkanolic acid. Preferably, the heptanoic acid will constitute from 25 to 75 mole % of the total amount of acids utilised in the synthesis, with the branched C₉ acid constituting the remainder. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

The second lubricant will typically be part of a lubricant composition which also comprises one or more of the additives which are conventional in the refrigeration lubricants art. Specific mention may be made of antioxidants, deacidifying agents and extreme pressure resistant agents. Such additives are well known to those skilled in the art.

Preferred antioxidants are the compounds containing a hindered phenol in the molecule, preferred deacidifying agents are the compounds containing an epoxy group in the molecule, and the preferred extreme pressure resistant agents are the phosphate and phosphite esters.

The following compounds are representative of the preferred antioxidants, deacidifying agents and extreme pressure resistant agents.

Antioxidants: 2,6-di-t-butyl-4-methylphenol,
2,6-di-t-butyl-4-ethylphenol,
2,6-di-t-butyl-4-hydroxyphenol,
2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-
5 methylenebis(4-ethyl-6-t-butylphenol),
2,2'-butylidenebis(4-methyl-6-t-butylphenol),
4,4'-butylidenebis(3-methyl-6-t-butylphenol),
1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane,
1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-
10 hydroxybenzyl)benzene and the like.

Deacidifying agents: Phenyl glycidyl ether,
butylglycidyl ether, bisphenol A epichlorohydrin
condensate, vinylcyclohexene dioxide,
2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxycyclohexane)-
15 meta-dioxane, 3,4-epoxycyclohexylmethyl-3,4-epoxy-
cyclohexane carboxylate, polypropylene glycol
diglycidyl ether, resorcin diglycidyl ether,
polyethylene glycol diglycidyl ether and the like.

Extreme pressure resistant agents: Tricresyl
20 phosphate, trisnonylphenylphosphite, distearyl
phosphate, tributylphosphate, trilaurylphosphate,
trilaurylphosphite, mono-di-mixed-lauryl phosphite,
mono-di-mixed-tridecyl phosphate, mono-2-ethylhexyl-
2-ethylhexylphosphate, di-2-ethylhexyl phosphate and
25 the like.

The volume of lubricant which is discharged from
the heat transfer device in accordance with the
replacement method of the present invention is normally
taken from the compressor. In many heat transfer
30 devices the compressor is equipped with a sump or
reservoir which at any one time contains a proportion
of the total lubricant circulating around the heat
transfer device. Conveniently, therefore, the volume of
lubricant which is discharged from the heat transfer

device in accordance with the replacement method of the present invention is that which is held within the sump. The sump will typically comprise some form of draining means which allows the lubricant to be readily removed therefrom.

Similarly, the second lubricant is normally charged to the compressor and where the compressor is equipped with a sump, the second lubricant will normally be charged to the sump.

Preferably, as much of the lubricant will be removed from the heat transfer device as is possible in step (a) prior to charging the second lubricant. The volume of the second lubricant which is charged to the heat transfer device will normally substantially equal the volume of the lubricant removed. Generally, both the removal of the lubricant and the charging of the second lubricant are effected while the heat transfer device is turned off.

In one embodiment of the present invention, after initially discharging a volume of the first lubricant from the heat transfer device and charging a volume of the second lubricant thereto, the device is restarted, with the first heat transfer fluid still in situ, and kept running for a period of time which is sufficient to homogenise the second lubricant with the residual first lubricant contained within the device. Effective homogenisation will usually require multiple circulations of the first and second lubricants around the device, and the total running time for the device will depend on the total volume of lubricant it contains, the volume of lubricant discharged and the rate at which the lubricant is circulated around the device. After this operation is complete, the heat transfer device contains a mixture of the first and

second lubricants, which may then be sampled and assayed to determine the residual level of the first lubricant.

5 The above described process of discharging a
volume of the lubricant from the heat transfer device,
charging a volume of the second lubricant, and running
the heat transfer device to homogenise the second
lubricant with the lubricant remaining in the heat
transfer device, may be repeated if the residual level
10 of the first lubricant contained in the heat transfer
device after the initial replacement operation is
unacceptable. Of course, after the initial replacement
operation the lubricant contained in the heat transfer
device is a mixture of the first and second lubricants,
15 and as successive replacement operations are completed
this lubricant mixture will become increasingly rich in
the second lubricant.

 In an alternative embodiment, after initially
discharging a volume of the first lubricant from the
20 sump and charging a volume of the second lubricant
thereto, the heat transfer device is restarted, with
the first heat transfer fluid still in situ, and kept
running for a period of time which is sufficient to
effect a single circulation of the second lubricant
25 within the device so that substantially all of the
first lubricant is ejected into the sump as a slug,
which is then discharged. By effecting only a single
circulation of the second lubricant, intimate mixing
between the first and second lubricants is discouraged,
30 and the second lubricant ejected from the compressor
tends to push the first lubricant along ahead of it
until the first lubricant reaches the sump for
subsequent discharge. Replacing the oil ejected into
the sump with a fresh charge of the second lubricant

may bring the concentration of the first lubricant to an acceptably low level in a single operation, although the above technique may be repeated if the oil circulating within the heat transfer device is too rich in the first lubricant.

In a further alternative, after first discharging the first lubricant within the sump and replacing it with a second lubricant, a substantial amount of the residual first lubricant is ejected as a slug by a single circulation of the second lubricant with the slug being suitably discharged, whereupon a further volume of the second lubricant is charged and homogenised with any remaining first lubricant to form a lubricant mixture. Subsequent discharging, charging and homogenisation may then be carried out as necessary.

Only when the residual concentration of the first lubricant remaining in the heat transfer device is at an acceptably low level is the first heat transfer fluid discharged and replaced with the second heat transfer fluid. An acceptable residual concentration of the first lubricant is achieved when the lubricant composition within the heat transfer device contains less than 10 % by volume, preferably less than 5 % by volume, more preferably less than 3 % by volume and particularly preferably less than 1 % by volume of the first lubricant, in that at or below these levels any adverse effect due to the precipitation of the first lubricant by the subsequent introduction of the fluoroalkane is negligible.

Commercially available recovery/reclaim units may be used to remove the first heat transfer fluid prior to charging the second heat transfer fluid. Such units typically comprise a vacuum pump and a container for

storing the first heat transfer fluid which is removed from the heat transfer device.

The present invention will now be illustrated, but not limited, by the following examples.

5

Example 1

10 In this Example, a glycol chiller containing chlorodifluoromethane (R-22) refrigerant and a mineral oil based lubricant was converted to operate with a fluoroalkane refrigerant blend comprising 30 % by weight difluoromethane (R-32), 10 % by weight pentafluoroethane (R-125) and 60 % by weight 1,1,1,2-tetrafluoroethane (R-134a), and "Emkarate" (TM) 15 RL-32S lubricant (see below). The chiller system comprised a Carrier 5H80 type open compressor, a direct expansion, air-cooled condenser and a direct expansion evaporator which acted to chill a secondary glycol refrigerant to 6°C.

20 As much of the mineral oil based lubricant was drained from the chiller system as was possible and replaced with a substantially equivalent volume of "Emkarate" (TM) RL-32S. The chiller was then restarted, with the R-22 refrigerant still in situ, in order to 25 homogenise the "Emkarate" (TM) RL-32S with the mineral oil lubricant remaining within the chiller. The above described process of discharging a volume of lubricant from the chiller, charging a volume of "Emkarate" (TM) RL-32S lubricant and running the chiller to homogenise 30 the "Emkarate" (TM) RL-32S with the lubricant remaining in the chiller was carried out three times, after which the residual concentration of mineral oil was less than 5 % by volume of the total volume of lubricant. Following replacement of the desiccant cartridge for 35

one compatible with R-134a, the R-22 refrigerant was discharged from the chiller and replaced with the R-32/R-125/R-134a refrigerant blend.

5 The performance of the chiller following conversion was found to be indistinguishable from that achieved during previous operation with R-22 in terms of compressor overall performance and refrigeration capacity. After 5 months of continuous operation under normal duty, the compressor was stripped and inspected. 10 The compressor parts displayed a level of wear that is comparable to that occurring when R-22 and mineral oil are used over a similar period of time. Analysis of the "Emkarate" RL-32S lubricant revealed no significant change in the levels of total acid number, metals (Cu, 15 Fe, Al), colour or viscosity.

"Emkarate" RL-32S is a commercially available ester based lubricant obtainable from ICI Chemicals & Polymers Ltd. Specifically, the lubricant comprises an 20 ester composition derived from pentaerythritol, heptanoic acid and a mixture of branched alkanolic acids having from 8 to 10 carbon atoms. "Emkarate" is a trade mark.

25 Example 2

In this Example, a glycol chiller based on a Bitzer 4P type semi-hermetic compressor with direct expansion evaporator and condenser units and containing 30 R-22 and a mineral oil based lubricant was converted to operate with a fluoroalkane refrigerant blend comprising 30 % by weight R-32 and 70 % by weight R-134a, and "Emkarate" (TM) RL-46S lubricant (see below).

As much of the mineral oil based lubricant was drained from the chiller system as was possible and replaced with a substantially equivalent volume of "Emkarate" (TM) RL-46S. The chiller was then restarted, with the R-22 refrigerant still in situ, in order to homogenise the "Emkarate" (TM) RL-46S with the mineral oil lubricant remaining within the chiller. The above described process of discharging a volume of lubricant from the chiller, charging a volume of "Emkarate" (TM) RL-46S lubricant and running the chiller to homogenise the "Emkarate" (TM) RL-46S with the lubricant remaining in the chiller, was carried out three times after which the residual concentration of mineral oil was less than 1 % by volume of the total volume of lubricant.

Following replacement of the desiccant cartridge for one compatible with R-134a, the R-22 refrigerant was discharged from the chiller and replaced with the R-32/R-134a refrigerant blend. After running the chiller for about 1 month, this refrigerant blend was replaced by one comprising 25 % by weight R-32 and 75 % by weight R-134a with no change to the lubricant charge. The chiller was then run for a further 1 month period, following which the refrigerant blend was replaced once more with a blend comprising 30 % by weight R-32, 10 % by weight R-125 and 60 % by weight R-134a, again without changing the lubricant. The performance of the chiller system with each of the three fluoroalkane refrigerant blends was compared to the performance of the same chiller system operating with R-22 and "Emkarate" RL-46S measured during the replacement procedure, and was found to be satisfactory in all cases. No changes to the viscosity, colour or metals content of the "Emkarate" RL-46S were observed.

"Emkarate" RL-46S is a commercially available ester based lubricant obtainable from ICI Chemicals & Polymers Ltd. Specifically, the lubricant comprises an ester composition derived from pentaerythritol, dipentaerythritol, heptanoic acid and branched alkanolic acids having from 8 to 10 carbon atoms. "Emkarate" is a trade mark.

10

15

20

25

30

35

Claims:

1. A method for replacing a first working fluid composition held within a heat transfer device by a second working fluid composition, wherein the first working fluid composition comprises a first heat transfer fluid and sufficient to provide lubrication of a first lubricant and the second working fluid composition comprises a second heat transfer fluid comprising at least one fluoroalkane and sufficient to provide lubrication of a second lubricant, which method comprises sequentially performing the steps
 - (a) discharging from the device a volume of a lubricant;
 - (b) charging to the device sufficient of the second lubricant to maintain lubrication;
 - (c) circulating the second lubricant within the device;
 - (d) optionally assaying the residue of the first lubricant within the device;
 - (e) repeating steps (a) to (d) as necessary until an acceptably low concentration of the first lubricant remains in the device; thereafter
 - (f) discharging from the device the first heat transfer fluid and charging to the device sufficient of the second heat transfer fluid to provide an adequate heat transfer effect.
2. A method as claimed in claim 1 wherein the first heat transfer fluid comprises chlorodifluoromethane or an azeotropic mixture of chlorodifluoromethane and chloropentafluoroethane.
3. A method as claimed in claim 1 or claim 2 wherein the second heat transfer fluid comprises at least one fluoroalkane selected from the group consisting of

difluoromethane, 1,1,2,2-tetrafluoroethane,
1,1,1,2-tetrafluoroethane, pentafluoroethane,
1,1-difluoroethane, 1,1,1-trifluoroethane and
1,1,2-trifluoroethane.

5 4. A method as claimed in claim 3 wherein the second
heat transfer fluid comprises a mixture of
1,1,1,2-tetrafluoroethane and difluoromethane.

5. A method as claimed in claim 3 wherein the second
heat transfer fluid comprises a mixture of
10 1,1,1,2-tetrafluoroethane, difluoromethane and
pentafluoroethane.

6. A method as claimed in any one of the preceding
claims wherein the first lubricant comprises a mineral
oil.

15 7. A method as claimed in any one of the preceding
claims wherein the second lubricant comprises a
polyoxyalkylene glycol.

8. A method as claimed in any one of claims 1 to 6
wherein the second lubricant comprises a neopentyl
20 polyol ester.

9. A method as claimed in claim 8 wherein the
neopentyl polyol ester comprises one or more compounds
of general formula:

25



wherein

30 R^2 is the hydrocarbon radical remaining after
removing the hydroxyl groups from pentaerythritol,
dipentaerythritol or trimethylol propane;

each R^3 is independently a linear alkyl group or a
branched alkyl group; and

35

n is an integer of 3, 4 or 6,

wherein one or more of the named polyols, one or more linear alkanolic acids, or esterifiable derivatives thereof, and optionally one or more branched alkanolic acids, or esterifiable derivatives thereof, are utilised in the synthesis of the ester.

10. A method as claimed in claim 9 wherein each R^3 is independently a C₄₋₇ linear alkyl group or a C₇₋₉ branched alkyl group.

11. A method as claimed in claim 9 wherein at least one acid selected from the group consisting of pentanoic acid, heptanoic acid and branched alkanolic acids having from 8 to 10 carbon atoms or an esterifiable derivative thereof is utilised in the synthesis of the ester.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number
GB 9314740.3

Relevant Technical fields

(i) UK Cl (Edition L) F4H (HGXJ)

(ii) Int Cl (Edition 5) F25B

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Search Examiner

M C MONK

Date of Search

26 AUGUST 1993

Documents considered relevant following a search in respect of claims **ALL**

| Category (see over) | Identity of document and relevant passages | Relevant to claim(s) |
|------------------------|--|-------------------------|
| | NONE | |

| Category | Identity of document and relevant passages .. - 31 - | Relevant to claim(s) |
|----------|---|-------------------------|
| | | |

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)